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Purification of U and Pu from Bulk Environmental Samples for Analysis by MC-ICPMS

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1.0 PURPOSE

This procedure gives the methods used at LLNL for the purification of uranium and plutonium from bulk environmental samples provided by the IAEA through the DOE Network of Analytical Laboratories (NWAL).

2.0 SCOPE AND APPLICATION

This procedure describes the separation and purification of uranium and plutonium from organic-rich bulk solid samples that are amenable to thermal decomposition (ashing). For example, it applies to most swipe materials (cotton, polyester), air filters (cellulose), and to vegetation. Alternative sample decomposition or pre-concentration methods must be used for glass fiber filters, and soil or water samples. However, after appropriate matrix-specific pre-treatment, the purification methods for U and Pu given here should be effective.

The procedure will yield separated U and Pu of sufficient purity for analysis of their isotopic composition by inductively coupled plasma mass spectrometry (ICPMS). These elements may not be pure enough for successful analysis by other methods, for example, thermal ionization mass spectrometry (TIMS). Additional purification steps prior to TIMS analyses are recommended.

3.0 APPARATUS AND MATERIALS

3.1 Quartz tubes, beakers and quartz wool

3.2 Muffle furnace capable of attaining 650º C

3.3 Plastic columns with 2 mL bed capacity (*e.g.*, BioRad, Poly-Prep)

3.4 Plastic columns with 0.3 mL bed capacity

3.5 PFA Teflon vials with screw tops, 14 mL capacity (*e.g.*, Savillex)

3.6 Hotplates and heat-lamps

3.7 Disposable plastic transfer pipets

3.8 Pen for writing on Teflon (Cryomarker)

4.0 STANDARDS AND REAGENTS

4.1 ASTM Type II reagent grade water (*e.g.*, Milli-Q water, 18 Mohms)

4.2 Ultra-pure (*i.e.*, sub-boiling distilled) concentrated hydrochloric (HCl), nitric (HNO_3), hydrofluoric (HF), and perchloric ($HClO_4$) acids (*e.g.*, Seastar Chemical Co.)

4.3 Hydriodic acid (HI), 55%, ACS reagent, unstabilized (*e.g.*, Sigma-Aldrich)

4.4 Saturated sodium nitrite solution ($NaNO_2$).

4.5 8 M HNO_3

4.6 3 M HNO_3

4.7 9 M HCl

4.8 0.1 M HCl

4.9 0.1 M HCl – 0.005 M HF

4.10 0.1 M HCl : concentrated HI, 15 : 1 mixture (prepared immediately prior to use)

4.11 9 M HCl : concentrated HI, 15 : 1 mixture (prepared immediately prior to use)

4.12 ^{233}U spike, of known isotopic composition and previously calibrated

4.13 Plutonium spike solution (^{242}Pu or ^{244}Pu), of known isotopic composition and previously calibrated

4.14 Anion Exchange Resin (BioRad AG1-X8, 100-200 mesh, chloride form)

4.15 EiChrom TEVA resin, selective extraction media

5.0 HEALTH AND SAFETY

This procedure describes activities authorized under Integrated Work Sheet (IWS) 11801 entitled “Sample Digestion and Preparation for B151 Mass Spectrometry”. Reggie Gaylord is the authorizing individual of this IWS for Chemistry & Materials Science, Chemical Biology & Nuclear Science Division, and Ross Williams is the responsible individual.

6.0 PROCEDURE

6.1 SAMPLE PREPARATION – SPIKING AND ASHING

6.1.1 Assign laboratory ID's to the client sample ID's and record in the logbook.

6.1.2 Label a new quartz tube with the laboratory ID and transfer the sample into the tube using new poly-gloves for each sample. Fold the swiped surface inward, remove the swipe from the plastic bag, fold again as necessary, and press the folded sample into the bottom of the tube. Place the sample tube in a quartz crucible or beaker to hold it upright.

6.1.3 Add appropriate amounts of ^{233}U and ^{244}Pu spike. For each set of similarly spiked samples, record the weight of the spike vial before and after spiking. Also record the spike ID, the volume of the spike added to each sample and identify the sample(s) to which the spike vial weights pertain. Dry the spiked sample by placing it in a beaker on a hotplate. Additional heating can be provided with a heat-lamp. Allow to cool and then plug each sample tube with a ball of quartz wool.

6.1.4 Place the sample in a muffle furnace **and map its position**. Dry ash using the following heating pattern as a guide. Strict adherence to this pattern is not necessary, except that the longer wait time at about 350º should be observed to allow the sample to char slowly. All temperatures are degrees centigrade. Ramp to 120º – wait 5 minutes, 250º – wait 10 minutes, 350º – wait one hour, 450º – wait 10 minutes, ramp to 650º and hold for two hours. Turn off the furnace and allow it to cool. **Re-label the sample with the laboratory ID as it is removed from the furnace.**

6.1.5 Remove and discard the quartz wool plug. Add approximately 5 mL of 8 M HNO_3 rinsing down the walls of the tube. Warm the sample tube by placing it in a dry beaker on a hotplate. Allow the sample to reduce in volume to less than 5 mL, but do not dry completely, and then cool.

6.1.6 Label a new PFA Teflon vial (14 mL size) and transfer the sample (solution plus solids if not dissolved) from the quartz tube to the Teflon vial. Rinse the tube with a few mL of 8 M HNO_3 plus 0.2 mL of concentrated HF, using a transfer pipet to rinse down the walls of the tube, and then transfer to the vial. Complete the transfer with a few more ml of 8 M HNO_3.

6.1.7 Add 0.1 mL of $HClO_4$ to the sample solution in the Teflon vial and take to dryness on a hotplate. Add about 5 drops of concentrated HNO_3 and dry again

6.2 U AND Pu PURIFICATION – ANION RESIN COLUMN: 8 M HNO_3

6.2.1 Prepare a 2 mL AG1x8 (100-200 mesh) anion exchange resin bed in a labeled BioRad poly-prep column. Remove bubbles from the resin bed and

condition with about 8 mL of Milli-Q H_2O followed and 12 mL of 8M HNO_3.

6.2.2 Dissolve the samples in 2 mL of 8 M HNO_3 plus 0.05 mL saturated $NaNO_2$ solution. Heat on a hotplate with caps on and cool in de-ionized H_2O in an ultrasonic bath. An additional 1 mL of 8 M HNO_3 may be added to samples that do not dissolve completely. These should be heated and cooled again, but if still not in solution, the sample should be transferred to a centrifuge tube and centrifuged to separate the sample in solution from the residue.

6.2.3 Label small plastic screw-top vials and position them under the conditioned columns to catch and save the waste solutions. Load the sample solutions on the conditioned columns. U and Pu adsorb and most contaminants pass. Rinse the vials with 2 mL of 8 M HNO_3 and load this on the resin bed as the first rinse. Allow this to pass and then load 2 mL of 8 M HNO_3 loaded directly on the column.

6.2.4 Rinse the Teflon vial that the sample was loaded from and position it under the column to catch the elution. Elute U and Pu together by loading 1 mL, 1 mL, and then 2 mL of 0.1 M HCl-0.005 M HF. Follow this with 2 mL, 2 mL and 2 mL of 0.1 M HCl:concentrated HI mixture (15:1). The HCl:HI reagent should be prepared fresh before use. The Teflon vial will contain approximately 10 mL of solution.

6.2.5 Dry the sample on a moderate hotplate. When the sample is dry and all the iodine has evaporated, indicated by the absence of colored fumes, add a few drops of concentrated HNO_3 and dry again. Then add a few drops of concentrated HCl and dry again. Rinse and dry the tops of the vials and cap the sample.

6.3 U SEPARATION FROM Pu – ANION RESIN COLUMN: 9 M HCl

6.3.1 Prepare a 1 mL AG1x8 (100-200 mesh) anion exchange resin bed in a labeled BioRad poly-prep column. Remove bubbles from the resin bed and condition with 4 mL Milli-Q H_2O water followed by about 6 mL of 9M HCl. Prepare another set of 14 mL Teflon vials labeled for the Pu fraction. The vials containing the sample will be used for the U fraction.

6.3.2 Dissolve the samples in 0.5 mL of 9 M HCl plus 10 ul HNO_3. Heat with caps on and cool in an ultrasonic bath. Load the sample solutions on the conditioned columns. Both U and Pu adsorb and most contaminants, including thorium, pass. Rinse the vials with 1 mL of 9 M HCl and load this on the resin bed as the first rinse. Allow this to pass and then load 2 mL of 9 M HCl directly on the column.

6.3.3 Place the Teflon vial to catch the Pu fraction under the column and elute the Pu with 6 mL of 9 M HCl : HI mixture (15 : 1). The HCl:HI reagent should be prepared fresh before use. Load this solution in 1 mL, 2 mL and 3 mL increments. Take the Pu fraction to dryness on a hotplate. When all the iodine has evaporated add a few drops of concentrated HNO_3 and dry again.

6.3.4 Rinse the initial sample vial and place under the column to catch the U fraction. Elute the uranium with 7 mL of 0.1 M HCl, loaded in 2 mL, 2 mL and 3 mL increments. Dry the uranium on a hotplate. When dry add a few drops of concentrated HNO_3 and dry again. Assuming that any residual spot in the Teflon vial is not milligrams of uranium, the spot should be very small. If so, the U fraction is ready for analysis. If not, the uranium fraction may need further purification.

6.4 Pu PURIFICATION – TEVA COLUMN: 3 M HNO_3

6.4.1 Prepare a small disposable column from a transfer pipet plugged with porous frit material and load with 0.3 mL of EiChrom TEVA resin. Check for and remove any air bubbles in the resin bed or below the frit, and condition the resin bed with 1 mL of Milli-Q H_2O followed by 2 mL of 3 M HNO_3

6.4.2 Dissolve the sample in 0.25 mL of 3 M HNO_3 plus 15 uL saturated $NaNO_2$. Warm on a hotplate and cool in an ultrasonic bath. Load the sample onto the column. Pu adsorbs and contaminants pass in the effluent. Rinse the resin with 0.25 mL then with 0.5 mL of 3 M HNO_3 passed through the vial, then rinse with 1 mL of 3 M HNO_3 loaded directly on the column.

6.4.3 Rinse the Teflon vial that the sample was loaded from and position it under the column to catch the elution. Elute Pu by adding 0.5 mL of 0.1 M HCl followed by 3 mL of 0.1 M HCl : HI mixture (15:1).

6.4.4 Dry the sample on a moderate hotplate. When all the iodine has evaporated, add a few drops of concentrated HNO_3 and 25 uL of $HClO_4$ and dry with assistance from a heat-lamp. Add a few drops of concentrated HNO_3 and dry again. The sample is ready for analysis